Glycerol Dry Reforming Over Alumina-Supported Nickel Catalysts

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Abstract

In this paper, dry (CO_2)-reforming of glycerol, a new reforming route was carried out over alumina (Al_2O_3)-supported non-promoted and lanthanum-promoted Ni catalysts. Both sets of catalysts were synthesized via wet co-impregnation procedure. The physicochemical characterization of the catalysts showed that the promoted catalysts possessed smaller metal crystallite size, hence higher metal dispersion compared to the virgin Ni/Al_2O_3 catalyst. This was also corroborated by estimations employing the Scherrer equation. In addition, modeling of gas-solid catalyst interaction from TGA analysis showed that the Order of Reaction model gave the best result with calcination energy ranged from 138 to 141 kJ mol^{-1} depending on the heating ramp. Preliminary reaction studies at 1023 K showed that glycerol dry reforming successfully produced syngas (H_2 and CO mixture) and the catalytic performance was stable for at least 4 h of reaction.

1. Background

The use of biodiesel as transportation fuel has spurred its burgeoning production; hence generation of plethora of glycerol as waste byproduct. One of the propositions to address the problem is by turning the waste into useful product such as syngas. In the current work, alumina supported nickel catalyst promoted with lanthanum in **various** compositions were synthesized and systematically characterized for the use in accelerating the rate of glycerol dry reforming (cf. Eq. (1)). Significantly, to the best of our existing knowledge, no prior works have been reported for this type of reforming system.

$$C_3H_8O_3 + CO_2 \rightarrow 4CO + 3H_2 + H_2O \qquad \text{Eq. (1)}$$

2. Methodology

Two sets of catalysts *viz*., 20wt%Ni/ 80wt%Al_2O_3 and La (1 to 5wt%)-promoted Ni/Al_2O_3 catalysts were synthesized from wet co-impregnation. Various catalyst characterization methods were carried out to determine the physicochemical properties, *i.e*. BET surface area, thermogravimetry analysis (TGA), XRD, FESEM-EDX and density measurements. Glycerine was purchased from Sigma Aldrich and directly injected into a 10-mm diameter fixed-bed reactor system at 1023 K. N_2 was applied as the carrier gas while H_2 was applied as catalyst activation agent. During the reaction, CO_2 reactant was individually added to the reactor. The produced syngas was analysed by gas chromatography.

3. Results & Discussion

3.1. Physicochemical characterization

Several physicochemical characterization analyses of synthesized catalysts were discussed in this section. Fig. 1 shows that pure calcined alumina sample possessed shorter and broader peaks consistent with γ-alumina phase. Significantly, the diffraction peak of alumina after impregnation with nickel (resulting in Ni/Al_2O_3 sample) has shifted to the lower 2θ values. This can be attributed to the diffusion of NiO into the support to form $NiAl_2O_4$ phase (Zangouei *et al*., 2010). For all the lanthanum (La)-promoted catalysts, it can be observed that the peaks representing $NiAl_2O_4$ phase at 2θ of 37.0°, 44.9° and 65.5° were obtained indicating near-similarity of La-Ni-Al_2O_3 interactions across different La loadings. Interestingly, La-dopant that exists as La_2O_3 species in La-promoted catalysts was undetectable from the XRD analyses. This is most likely because La^{3+} is a large ion and therefore difficult to diffuse into the support's vacant sites. Consequently, La exists as La_2O_3 with high dispersion within the solid matrix. Subsequently, the peak intensities especially the NiO peak at 2θ of 43.5° has decreased with La content because NiO and $NiAl_2O_4$ were dispersed by La_2O_3 dopant, hence smaller crystallite size (cf. Table 1).

Table 1: Crystallite Size of NiO

Catalysts	Ni/Al_2O_3, (N/A)	1%La-N/A	2%La-N/A	3%La-N/A	4%La-N/A	5%La-N/A
Crystallite Size, Å	128	130	110	91	Undetectable	Undetectable

Solid-gas interaction during calcination stage was examined from TGA analysis and kinetic behaviour corresponds to the NiO phase (derivative weight results not shown here) was fitted to the existing models (Brown, 1977). Table 2 shows the modelling results. Discrimination of results based on regression coefficients (R^2) and magnitude of calcination energy (E_A) representing kinetic region concluded that model "F3" was adjudged the best model. The E_A has also decreased with heating ramp (cf. Table 2).

Table 2: Modelling results for NiO phase formation

Models		10K/min		15K/min		20K/min	
		Ea, KJ/mol	R^2	Ea, KJ/mol	R^2	Ea, KJ/mol	R^2
Nucleation Models	A2	20.9841	0.7665	22.2361	0.7543	22.9250	0.7807
	A3	10.8651	0.6577	11.6997	0.6503	12.1589	0.6862
	A4	5.80559	0.4864	6.43147	0.4927	6.7758	0.5398
Geometrical Contracting Models	R2	38.7044	0.7071	41.4964	0.7026	42.9756	0.7305
	R3	42.4024	0.7515	45.1261	0.7436	46.5887	0.769
Diffusion Models	D1	69.5492	0.5625	75.3163	0.654	78.2335	0.6828
	D2	79.2439	0.711	84.9590	0.7076	87.9445	0.7339
	D3	94.1779	0.791	99.6253	0.7818	102.5508	0.8035
	D4	83.9870	0.7398	90.3763	0.7332	92.6040	0.7581
Order of Reaction Models	F1	51.3414	0.835	53.8454	0.8223	55.2233	0.8418
	F2	90.2750	0.9442	91.4727	0.939	92.1953	0.9458
	F3	140.1776	0.9323	139.6452	0.9345	139.4733	0.937

3.2. Glycerol Dry Reforming Studies

Fig. 2 shows the transient composition profiles for preliminary reaction of glycerol dry reforming carried out at 1023 K. This behaviour was typical of other feed compositions over 20-wt%Ni/ 80-wt%Al_2O_3 catalyst. Blank tests using the same feed with either an empty reactor or calcined Al_2O_3 (support) bed yielded negligible glycerol conversion. This suggests that neither homogeneous gas phase glycerol dry reforming nor reaction over sites on the calcined support occurred at detectable rates. Glycerol conversion for the reaction shown in Fig. 2 gave a conversion X_G of approximately 52%. It is also apparent from the Fig. 2 that steady-state was attained for H_2 after about 1 h on-stream while CO reached this value after about 180 min.

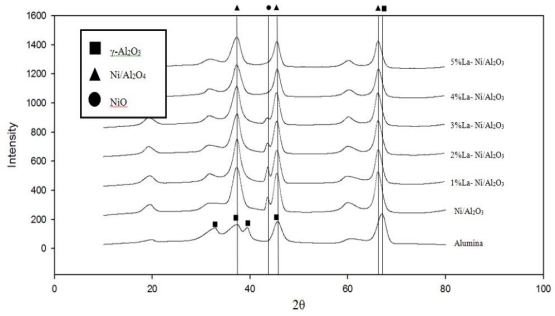

Figure 1: XRD Pattern of Prepared Catalysts

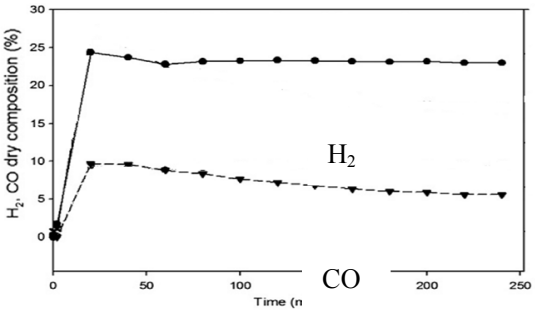

Figure 2: The Transient Composition Profile

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